PARAMETRIC STUDIES ON SYNTHESIS OF BIS(4-CHLOROBENZYL) SULFIDE USING HYDROGEN SULFIDE

A Thesis submitted for the award of the degree of

Bachelor of Technology

In

Chemical Engineering

Under the guidance of: ***Prof. Sujit Sen***

Submitted by: ***Dilip Pratap Singh***

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA- 769008

May 2015

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

CERTIFICATE

This is to certify that this thesis entitled as "*PARAMETRIC STUDIES ON SYNTHESIS OF BIS(4-CHLOROBENZYL) SULFIDE USING HYDROGEN SULFIDE"* submitted by DILIP PRATAP SINGH (111CH0506) in partial fulfilment of the prescribed curriculum of Bachelor of Technology degree in Chemical Engineering in session 2014-15 at National Institute of technology, Rourkela. This an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter put in the thesis by him is his original work.

Date:

Dr. Sujit Sen

Department of Chemical Engineering

ACKNOWLEDGEMENT

I take this opportunity to express my sincere thanks toward everyone who motivated me, inspired me and helped me in successful completion of my undergraduate research project (2014-15). I specially thank **Prof. Sujit Sen** to be so calm and helpful throughout the course of my project. The guidance of Prof. Sen has been very helpful and productive in my entire project work.

I also want to thank Prof. P Rath, Head of department of Chemical Engineering, to encourage me to do this project for the betterment of research and technology of NIT Rourkela. I also express my sincere gratitude to Gaurav Singh (Phd, Chemical Engineering,NIT Rourkela) and Devipriya Gogoi (M Tech., Chemical Engineering, NIT Rourkela) to provide a helping hand throughout the course of my Research project.

DILIP PRATAP SINGH

111CH0506

LIST OF FIGURES

LIST OF GRAPHS

TABLE OF CONTENTS

ABSTRACT

This study focuses on the utilization of Hydrogen Sulphide (H_2S) for the synthesis of Bis(4-chlorobenzyl)sulfide and Chlorobenzyl Mercaptan (CBM). This involves the absorption of H_2S in Methyl Diethanolamine and then reaction of this H_2S- rich Methyl diethanolamine with Chlorobenzyl Chloride for the synthesis of Bis(4-chlorobenzyl)sulfide and CBM. MDEA and Chlorobenzyl Chloride are two different phases and their reaction is very difficult to occur. So, to carry out the above reaction a phase transfer catalyst (PTC) has been used. The Ethyl Triphenyl Phosphonium Bromide (ETPB) has been used as the phase transfer catalyst. The objective of this work is to maximize the conversion of Chlorobenzyl Chloride and maximize the selectivity of Bis(4-chlorobenzyl)sulfide. In this project, Chlorobenzyl Chloride has been used along with Toluene as a solvent. Reaction time, catalyst loading, stirring speed, temperature and concentration of Chlorobenzyl Chloride are chosen as parameters.

Keywords: Hydrogen sulphide, Bis(4-chlorobenzyl)sulfide, Phase Transfer Catalyst, selectivity, conversion.

CHAPTER 1

INTRODUCTION

CHAPTER 1
INTRODUCTION

The present work gives a glimpse of the present day research and its validity. It acknowledges the introduction of the sources of Hydrogen Sulfide, its need for recovery and its utilization to synthesize fine chemicals.

1.1 SOURCES OF HYDROGEN SULPHIDE

Comprehensively, close around 10 percent of Hydrogen Sulfide emanation can be ascribed to human exercises. Various courses of action being carried on in the petroleum and coal industries lead to the generation of gaseous by products with Hydrogen Sulfide dissolved in it (Hydrogen sulfide: Overview, National Pollutant Inventory, Australia). Hydro desulfurization uoto a great extent is an acknowledged process in industries to make sulfur free characteristic gas. Petroleum refineries are one of the biggest mechanical asphalts for Hydrogen Sulfide in this way. Anyway, continuously its getting burdensome to cater light and simple to process unrefined petroleum and as an outcome sufficiently apparent, refiners everywhere throughout the globe are left with no other alternative aside from handling substantial rough with taking off substance of sulfur and nitrogen in it. Natural concerns and stringent measures for the same have constrained the refiners to hydro-treat such rough to change the sulfur and nitrogen fixations to the set levels. Hydro treatment of substantial rough further delivers huge bits of Hydrogen Sulfide and Ammonia.

Coal preparing businesses additionally include forms in charge of the outflow of Hydrogen Sulfide and Ammonia .The coal gas veritably has 0.3-3% Hydrogen Sulfide content and around 1.1% of NH_3 substance as the major non-hydrocarbon corrupt. The measure of Hydrogen

Sulfide of specific gas streams in common gas industry is dreadfully high to get business gesture. The measure of Hydrogen Sulfide in characteristic gas differs between 0.1 ppm to 150,000 ppm.("HYDROGEN SULFIDE" . Agency for Toxic Substances and Disease Registry.) Coke broilers, tanneries and paper factories are alternate wellsprings of Hydrogen Sulfide emerging out of the broadening of human exercises.

1.2 NEED FOR TREATING H_2S

Employers must ensure workers are not exposed to H_2S levels above the occupational exposure limit (OEL). The OEL is the level of an airborne substance that workers may be exposed to without wearing protective equipment, and without normally suffering adverse health effects.

A little bit at a time yet mass increment in ecological concerns has brought mounts of issues for substance commercial ventures with respect to the throwing out of unsafe materials like Hydrogen Sulfide in a satisfactory way. The enormous requirement for the expulsion of Hydrogen Sulfide from liquid streams has developed for safety issues. Hydrogen Sulfide being an extremely lethal gas with 4.3%-46% blast breaking points furthermore being heavier than air gathers at the base in spots not having fitting ventilation. It is an extremely unsafe gas as it sheds off its exceptional sharp smell rapidly leaving the victimized people clueless about the approaching threat of its blast. So keeping in mind the end goal to guarantee wellbeing measures a Hydrogen Sulfide Material Datasheet (MSDS) ought to be counseled. Gas streams must be

made totally free from H_2S before utilization and transportation attributable to its odiferous, destructive and noxious nature. Numerous pipelines stipulate the degree of H_2S to be underneath 0.25g/100 ft3 of gas. The vicinity of H_2S in the refinery gas streams can upset the back courses of action, for example, gear debasement, deactivation of catalyst, undesirable side reactions etc.

1.3 INDUSTRIAL PROCESS FOR THE REMOVAL AND RECOVERY OF H_2S

Commercial ventures need to diminish the hydrogen sulfide outflow beneath as far as possible to guarantee ecological security and wellbeing security for their laborer. Numerous modern procedures have been produced for the evacuation and the recuperation of H_2S.The acidic nature of H_2S can be utilized for its removal and recuperation by utilizing soluble arrangement. Solid soluble arrangement like sodium hydroxide frames irreversible synthetic response items and thus can't be utilized for the expulsion of hydrogen sulfide from the gas streams particularly if the gas contains both hydrogen sulfide and carbon dioxide where the CO_2 focus is more than 4% (Robin,1999). Along these lines, feeble soluble arrangements are utilized for the evacuation and recuperation of the H_2S.

1.3.1 AMMONIA BASED PROCESS

Utilization of fluid alkali in evacuation of hydrogen sulfide had been all around rehearsed (Hamblin,1973 and Harvey and Makrides,1980). The utilization of alkali to evacuate hydrogen sulfide and carbon dioxide from gas streams has declined lately, yet this methodology is utilized for desulphurising coke stove gas .The fundamental operation in the evacuation of H_2S gas is :

Gas stream containing both H_2S and NH_3 is made to go through a H_2S and a NH_3 scrubber set in series.NH_3 scrubber is encouraged with stripped water from the top where smelling salts is assimilated from the gas. The subsequent ammoniacal arrangement is utilized as permeable as a part of H_2S scrubber. The arrangement from this unit contains ammonium sulfide, which is disintegrated in deacidifier to deliver hydrogen sulfide and ammoniacal alcohol. The reactions occurring in this process is as shown:

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$NH_3 + H_2S \rightarrow NH_4HS$$

$$2NH_3 + H_2S \rightarrow (NH_4)_2S$$

Some of the advantages of ammonia based process over the ammine based process are:

- ✓ Ammonia salts based methodology is ideally equipped for gas streams containing both H_2S and NH_3. The evacuation of ammonia and hydrogen sulfide is done in single venture in alkali process and in two stages in alkaolamine based process.
- ✓ When gases containing both CO_2 and H_2S are contacted with aqueous ammonia solution, the H_2S is absorbed more rapidly.

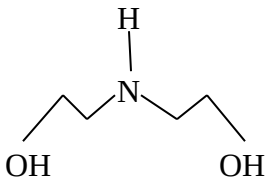
The operational troubles connected with the ammoniacal scrubbing has confined the utilization of this procedure as favored strategy for the removal of hydrogen sulfide. Some of the of the operational troubles connected with this methodology (Hamblin,1973) are:

- ✓ High partial pressure of ammonia forces the scrubbing to be led with relatively weaken NH_3 arrangement or at moderately high pressures or a different water wash step after the NH_3 cleaning step so as to remove ammonia from the treated gas stream. The recovery expense is expanded with the utilization of dilute scrubbing solutions as it is conducted at higher temperatures.
- ✓ The recovery of rich absorbent solution withdrawn from the scrubbing step includes the utilization of soluble catalysts, so sulfur item gets contaminated with the catalyst

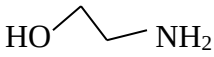
1.3.2 ALKANOLAMINE BASED PROCESS

Alkanolamine process has got wide acknowledgement in light of the fact that it has favorable element of low vapor pressure. The low vapor pressure makes the operation flexible as far as operatng pressure, temperature and concentration.

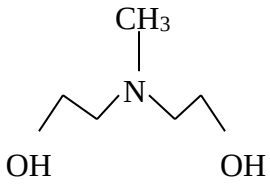
Triethanolamine(TEA), the first alkanolamine to be utilized in early scheduled gas treating plants (Bottoms,1930). Some of the amines that have been utilized are monoethanol amine(MEA), di-ethanolamine(DEA) and methyldiethanol amine(MDEA).MEA and DEA are not selective for H_2S in their reactions. The alkanolamine absorbs every single acid gas parts in the gas stream. For example, CO_2 and H_2S.



Di Ethanolamine



Mono ethanolamine



Methyl diethanolamine

Fig 1.1: Structural formulas of alkanolamines

Structural formulas for some of the alkanolamines are demonstrated above. Each has atleast one hydroxyl group and one amine group. The hydroxyl group serves to decrease the vapor-pressure and expand the water solubility, while the amine group gives the vital alkalinity in water so that the acidic gasses gets absorbed. The absorption reaction happens in absorber and afterward stripping of absorbed gasses happens in stripping column. The concentrated H_2S gas is then sent to sulfur recovery. The basic flow diagram graph of the amine-based acid gas evacuation methodology is demonstrated in figure1.2. Treatment with alkanolamine includes the flow of gas stream upward through the absorber, countercurrent to the stream of aqueous alkanolamine solution. The rich solution from the base of the absorber is heated by the heat exchanger with lean solution from the base of the stripping section where the absorbed gasses are stripped of from the alkanol amine solution. The recovered alkanol amine is then reused to the absorber. The concentrated hydrogen sulfide gas acquired from top of the stripping column is then sent to Sulfur recovery and disposal.

1.3 RECOVERY OF SULPHUR FROM HYDROGEN SULPHIDE

1.4.1 CLAUS PROCESS

The Claus process is the most significant gas desulfurizing process, recuperating elemental sulfur from gaseous hydrogen sulfide. Initially patented in 1883 by the researcher Carl Friedrich Claus, the Claus process has turned into a industry standard.

The multi-step Claus process recoups sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gasses containing hydrogen sulfide got from refining crude petroleum and other mechanical processes. The by-product gasses mostly release from physical and natural gas treatment units (Selexol, Rectisol, Purisol andamine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gasses might likewise contain hydrogen cyanide, hydrocarbons, sulfur dioxide or alkali.

Gasses with a H_2S substance of more than 25% are suitable for the recovery of sulfur in straight-through Claus plants while alternate designs, for example, a split flow set up setup or feed and air preheating can be utilized to process leaner feeds.

Hydrogen sulfide produced, for instance, in the hydro-desulfurization of refinery naphthas and other petroleum oils, is changed over to sulfur in Claus plants. The general main reaction is:

$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$ (1)

By the way, the greater part of the 64,000,000 metric tons of sulfur created worldwide in 2005 was by product sulfur from refineries and other hydrocarbon transforming plants. Sulfur is utilized for producing sulfuric acid, medicine, cosmetics, manures and elastic items. Basic sulfur is utilized as fertilizer and pesticide.

DESCRIPTION OF CLAUS PROCESS

Hydrogen Sulfide gas is advanced in the Claus unit in the wake of being seperated from the host gas using amine extraction. In this unit, the gas undergoes 2 stages:

1. Thermal Step:- The gas imbedded with hydrogen sulfide reacts in a substoichiometric ignition with air in a reaction furnace at a high temperature (1000-14000 'C).Now the claus gasses with the main flammable substance "H2S" is burnt in burner by the given chemical raction

$2H_2S + 2\ O_2 \rightarrow SO_2 + 2H_2O + S$ (2)

This includes a complete flame free oxidation of H_2S producing Sulfur Di Oxide. One third of all H_2S is changed over to sulfur di oxide in air to acid gas proportion.

2. Synergist Step:- In this step, the reaction gasses leaving the Sulfur condenser are heated again to 200-350 degree celcius and are put into a series of catalytic converter and sulfur condenser where a reaction happens in between of H_2S and SO_2 to produce natural sulfur:

$$2\ H_2S + SO_2 \rightarrow 3S + 2H_2O \quad (3)$$

A certain amount of H_2S deposit stays in the tail gas which alongside other trace sulfur compounds is dealt in the tail gas unit. This can give an appreciable sulfur recovery of around 99.8% which can further be advanced to a few different uses like manufacturing medicines, cosmetics, fertilizers etc.

But, the Claus process has some specific disadvantages in it (Plummer, 1994 and Plummer and Beazley, 1986). Some of them are:

- ✓ It works at high temperature
- ✓ It requires precise process control over oxygen and H_2S proportion.
- ✓ The tail gas discharged in the Claus process has high sulfur content, unsuitable to environmental concerns and regulations

1.4 PHASE TRANSFER CATALYST

Phase transfer catalysis (PTC) utilizes reactant measures of phase transfer agents which facilitate interphase transfer of species, making reactions between reagents in two immiscible phases (Schuster, R. E.; Scott, J. E. (1973). "Methyl isocyanide"). *Org. Synth.* PTC is used generally as a part of the combination of various organic chemicals in both liquid-liquid and solid-liquid systems. Existing literature on PTC is chemistry intensive and a mere bunch of recent articles constitute the entire information on engineering analysis. This article reviews the field comprehensively by consolidating the current information from chemistry with bits of knowledge into mechanistic and kinetic analysis and mathematical modeling of soluble and insoluble PTC. By its very nature, PTC includes a series of equilibrium and mass-transfer steps, besides the two principle reactions. Disregard of mass-transfer impacts can terribly over predict the conversion of a PTC catalyzed reaction. A practical method for using PTC, which empowers easy separations, is to immobilize the catalyst on a strong backing. Mass-transfer constraints and higher expenses, have blocked its commercial use as such, requiring further examination of mass transfer restrictions in these complex three phase systems. The use of PTC, consolidated with other rate enhancement methods like sonochemistry, microwaves, electro-organic synthesis, and photochemistry, is being increasingly explored. Applications here in this area in the manufacture of organic intermediates and fine chemicals appear to be practically boundless. (Mieczyslaw Makosza (2000). "Phase-transfer catalysis. A general green methodology in organic synthesis". *Pure Appl. Chem.* **72** (7): 1399–1403.).

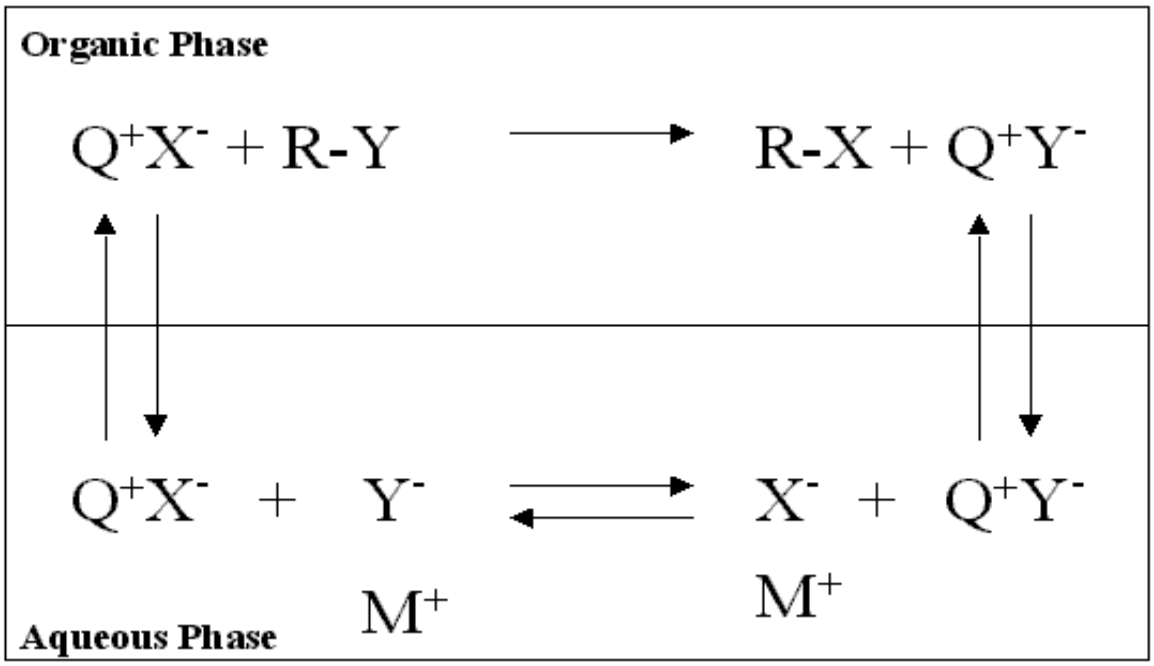


Fig. 1.2 SIMPLE MECHANISM OF PTC

Interfacial and extraction mechanisms are essentially used to detail the liquid-liquid phase transfer catalysis in view of the lipophilicity of the quaternary cation. The extraction mechanism propounded by starks is connected to low lipophilic catalysts, for example, benzyl triethylammonium and tetrabutyl ammoniun salts. The interfacial mechanism permits the catalysts, for example, tetrahexylammonium and trioctylmethylammonium to stay in the organic phase just attributable to their high lipophilicity. In this phase anions are likewise exchanged over the liquid-liquid interface.

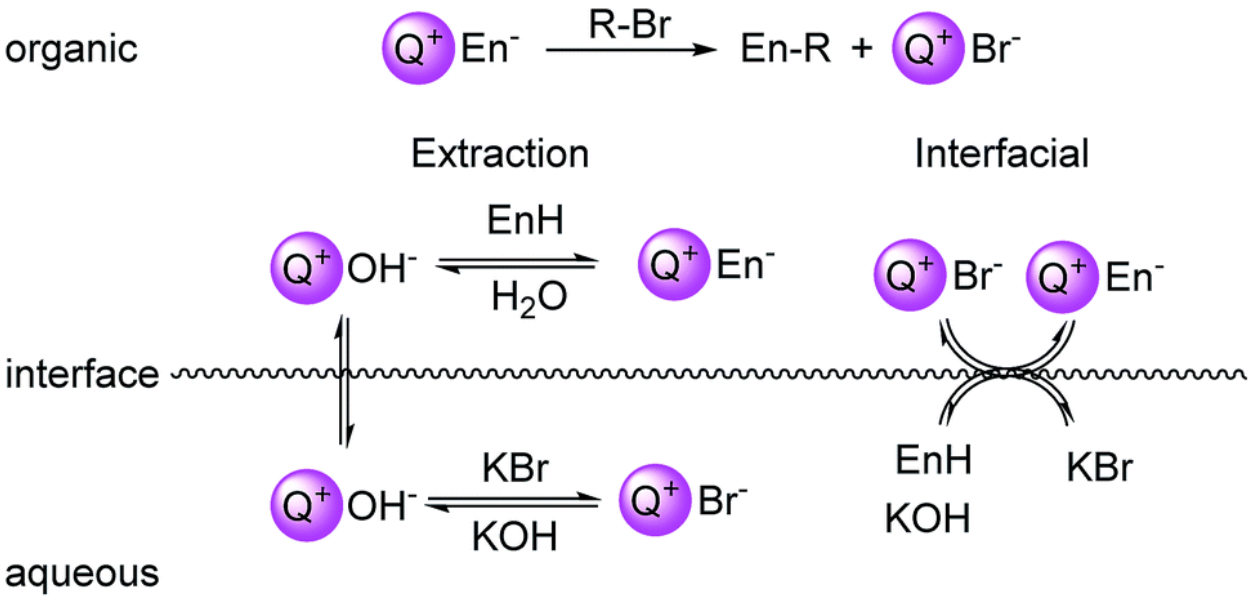


Fig. 1.3 INTERFACIAL AND EXTRACTION MECHANISM

The aqueous phase used is methyl diethanol amine. It has got some of the advantage. They are as per the following:

• The MDEA has low molecular weight that outcomes in high solution absorption at moderate concentrations.

• High alkalinity.

• It can be effectively recovered from the contaminated solution.

MDEA has got a percentage of the inconveniences also.They are:

• Selective absorption of H_2S is impractical, if gas stream has both CO_2 and H_2S.

• The MDEA solutions are more corrosive than other amines.

• High heat of reaction with H_2S prompts higher energy requirement for stripping.

1.5 PRESENT WORK

The present work is a substitute to the Claus methodology went for the ideal use of H_2S found in different gas streams. This account deals with the process of value addition to the chemicals which use the H_2S found in different by-product gas streams. Keeping in view the present process, the generation of value added chemicals can be credited to H_2S rich liquid ammonia salts. Present work can be committed to:

• Emphasis upon the effect of process variables (catalyst loading, temperature variation and concentration of reactant) on the adjustment in condition of organic reactants.

• Formulate an apt and an operational mechanism which can ideally use the effects of different parameters on the rate of reaction and conversion so that the course of reaction can be put forward in an productive manner.

CHAPTER 2

LITERATURE REVIEW

2.1 RECOVERY OF SULFUR FROM H_2S

Sulfur-bearing compounds are exceptionally detrimental to nature and to mechanical process equipment. They are regularly acquired or formed as a by-product of separation and thermal processing of fuels containing sulfur, for example, coal, raw petroleum and natural gas. The two sulfur compounds, which require extraordinary consideration, are: hydrogen sulfide (H_2S) and sulfur dioxide (SO_2). H_2S is a profoundly destructive gas with a foul odor, whereas. SO_2 is a dangerous gas in charge of acid rain formation and equipment corrosion. Different strategies for decreasing pollutants containing sulfur are portrayed in this paper, with an emphasis on the modified Claus process, improved by the utilization of High Temperature Air Combustion (HiTAC) innovation in the Claus furnace. The Claus process has been known and utilized as a part of the industry for more than 100 years. It includes thermal oxidation of hydrogen sulfide and its reaction with sulfur dioxide to form sulfur and water vapor. This procedure is equilibrium-limited and usually attains efficiencies in the scope of 94-97%, which have been viewed as worthy in the past years. These days, strict air contamination regulations in regards to hydrogen sulfide and sulfur dioxide discharges call for almost 100% productivity, which must be accomplished with process changes. High temperature air combustion technology or generally called flameless (or colorless) combustion is proposed here for application in Claus furnaces, particularly those utilizing lean acid gas streams, which can't be burned without the utilization of auxiliary fuel or oxygen enrichment under standard conditions. With the utilization of HiTAC it has been indicated, then again, that fuel-lean, Low Calorific Value (LCV) energizes can be smoldered with exceptionally uniform thermal fields without the requirement for fuel enhancement or

oxygen addition. The uniform temperature distribution supports clean and effective burning with an extra focal point of significant reduction of NOx, CO and hydrocarbon emission.

1.2 SYNTHESIS OF BENZYL MERCAPTAN AND BENZYL CHLORIDE MERCAPTAN

Benzyl mercaptan is utilized for the manufacture of herbicides of the thiocarbamate family (Labat, 1989). It is chiefly utilized for the synthesis of esprocarb, prosulphoarb, tiocarbazil and numerous more.

Hoffman and Reid (1923) synthesized BM by reacting benzyl chloride with ethanolic arrangement of liquid sodium sulfide (melted at 90^0C) soaked with hydrogen sulfide (H_2S). The solution was allowed to remain at low temperature,and shaking was proceeded for 4 days.

Heather (1988) synthesized BM by reacting benzyl chloride with sodium hydrosulfide in the two-stage conditions under H_2S air at a temperature of around 50 ^{0}C until roughly 90% of the starting material was changed over to BM (mixed for about 5 hours), then temperature was expanded by around 30 ^{0}C more for the balance of the reaction (for more 1.5 hours blending was done).

Bittell and Speier (1978) made BM by utilizing an solution of NH_3 and methanol soaked with H_2S at 0^0C. Benzyl chloride was added to this methanolic ammonium hydrosulfide (NH_4SH) arrangement at 0^0C while gradually bubbling H_2S through the solution. It took around 1 hr for the reaction to complete; BM (92%) and DBS (8%) was delivered.

Labat(1989), reacted benzyl chloride and ammonium hydrosulphide in a molar proportion of 1 in a closed reactor in two stages for the preparation of benzyl mercaptan. The first step included the addition of benzyl chloride to a hydrosulphide below 800^0C .In the second step, the reaction mixture was heated at around 800^0C to 1000^0C for 2hours.

In the present work, we react 4- Chlorobenzyl Chloride with Aq. MDEA to synthesize Bis(4-chlorobenzyl)sulfide and Chlorobenzyl Mercaptan(CBM). This product has got its application in paint industry and dyes.

1.5 SYNTHESIS OF DIBENZYL SULFIDE AND BIS(4-CHLOROBENZYL)SULFIDE

Di-benzyl Sulphide (DBS) is used as an added substance for extreme pressure lubricants, in refining and recovery of valuable metals, in different anti corrosive formulation, anti wear additive substances for engine oils, stabilizers for photographic emulsions(Pradhan and Sharma, 1990).

Pradhan and Sharma(1990), delivered DBS and para chlorobenzyl sulfide by reacting separate chlorides with sodium sulfide utilizing different catalyst under liquid liquid and solid liquid mode. Out of the six catalysts they attempted, TBAB(Tetra Butyl ammonium bromide) was discovered to be the best. In 1992,they likewise contemplated the reactions of nitrochlorobenzene with sodium sulfide in the vicinity and absence of a phase transfer catalyst and found that the solid liquid reaction is kinetically controlled in the vicinity of catalyst and is mass transfer controlled without catalyst.

The kinetics of reduction of nitro toluenes by aq. ammonium sulfide under Liquid-Liquid PTC with the utilization of (TBAB) as PTC was likewise examined (Narayan C Pradhan, Anand V Patwardhan, Sunil K Maity, 2006). The reaction of benzyl chloride with ammonium sulfide under LL PTC utilizing TBAB as PTC was additionally examined.

DBS was produced by reacting benzyl chloride and aq. ammonium sulfide utilizing TBAB as phase transfer catalyst. The parametric study was done on the selectivity of DBS. It was observed that DBS can be specifically prepared by keeping high benzyl chloride conc., High NH3/H2S proportion (Sujit Sen, Patwardhan, S K Maity, N C Pradhan, 2007).

The reaction of BC with H_2S rich MEA solution under Liquid-Liquid PTC was examined by Sujit Sen, N.C.Pradhan and Patwardhan(2010). It was discovered that higher proportion of MEA/H2S favored the development dibenzyl sulfide and if the proportion is lower it supports the formation of benzyl mercaptan. TBAB impetus was utilized.

Bis(4-chlorobenzyl)sulfide is formed when we react Chlorobenzyl chloride and H_2S rich MDEA solution in the presence of Phase Transfer Catalyst (ETPB). It was found that higher proportion of MDEA/H_2S favored the formation of Bis(4-chlorobenzyl)sulfide and if the proportion is lower it supports the formation of Chlorobenzyl mercaptan. ETPB catalyst was utilized.

1.6 PHASE TRANSFER CATALYST

In the late sixties, the Phase transfer technique showed up as another technique for overcoming issues of mutual solubility and offering the potential for activation of anions. The catalytic nature of this technique additionally introduced the guarantee of significant cost savings over more traditional methodologies (Makwza, M.,and Serafinovs,H.,Rocr. Chem., 39,1223 (1965))The fundamentals of the phase transfer technique are probably best comprehended by the consideration of a particular example. It was noted ahove that I -chlorooctane is inert to heating with concentrated aq. sodium cyanide solution (2,6). It was discovered that if. rather than the insoluble salt sodium cyanide, a natural dissolvable cyanide source, for example, tetrabutyl ammonium cyanide was used in this reaction, the sought change happened quickly and in great yield.

Quaternary ammonium salts, for example, tetrahutvlammonium chloride' give a source of an independently charged lipophilic cation. It should be noted, in any case, that not all quaternary ammonium cations serve viably as Phase transfer catalysts (Landini. D., Montanari, F., and Piriri, F. J.. J. Chem Sm.. Cham.1974).Tetramethylammonium cation is not lipophilic and to manage the cost of a noteworthy reaction rate in nucleophilic two-stage systems. Tetrahutylammonium iodide and hisulfate offer the advantage that they may be obtained in a high state of purity. . It has been broadly adopted that the pure compound is readily accessible and because of this they are considerable for its use.

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL

This chapter deals with the detailed procedure followed in experimental studies of the project. It includes chemicals used, equipment details, preparation of several reagents, experimental method, analysis, conclusion and discussion.

3.1 CHEMICALS

- ✓ Toluene(≥99.5%) was obtained from RFCL Limited, New Delhi.
- ✓ Ethyl Triphenyl Phosphonium bromide (ETPB) was obtained from Merck specialities Pvt. Ltd., Mumbai.
- ✓ Methyl diethanol amine (≥98%) was procured from LOBA CHEMICAL Pvt. Ltd., Mumbai.
- ✓ Synthesis grade Chlorobenzyl chloride (≥99%) was obtained from Merck(India) Ltd., Mumbai. \

3.2 EQUIPMENT

All the reactions were done in a mechanically agitated glass reactor of capacity 250cm^3. A 2cm width ,4 bladed turbine impeller was utilized for mixing the reaction mixture. The stirrer was

kept at a height of 1.5cm (approx.) from the base of reactor and it was having the provision for rate control. The reactor was kept in a water bath so that a fixed temperature can be kept in the system. The schematic chart is as demonstrated in the figure 3.1.

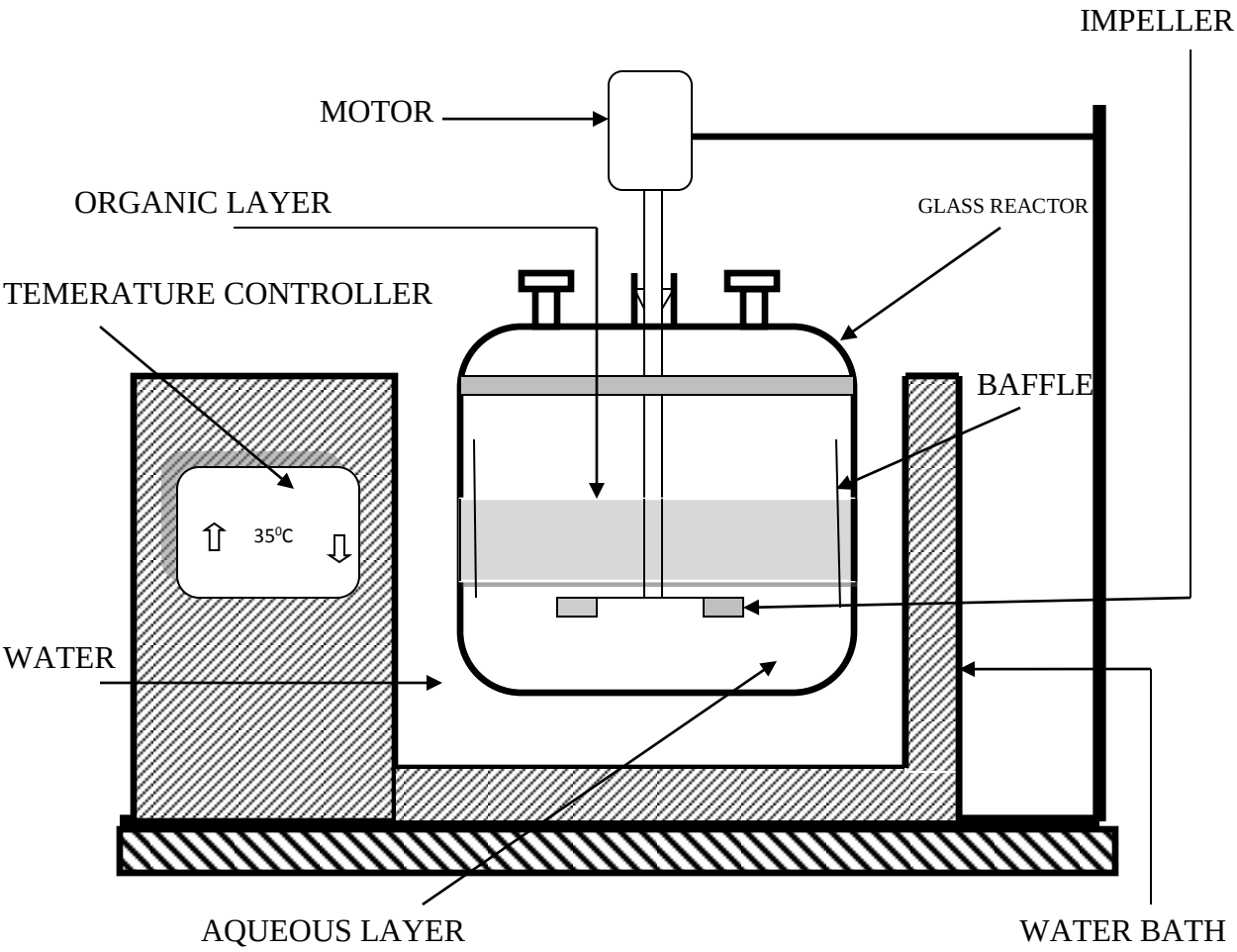


Fig 3.1: Schematic diagram of a batch reactor

3.3 PREPARATON OF H_2S RICH METHYL DIETHANOL AMINE

Firstly, H_2S gas was prepared by reacting FeS with H_2SO_4.The convergance of H_2SO_4 was taken as 1 molar. Then, around 30-35 wt% of MDEA arrangement was arranged by mixing appropriate amount of MDEA and distilled water. At that point the H_2S gas created in the kipp's apparatus was bubbled in the MDEA arrangement in a gas bubbler.

$$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$$

Since, the reaction of H_2S and MDEA solution is exothermic (Kohl and Nielsen, 1997), the gas bubbler containing MDEA solution was kept immersed in ice bath to prevent the oxidation of sulfide and to build the absorbance in MDEA arrangement as absorbance increments with reduction in temperature. The unabsorbed H_2S gas from the first bubbler was sent to second gas bubbler containing MDEA arrangement so that the H_2S gas is vented out under recommended environmental standards. At the point when the gas bubbling stops, the H_2S rich MDEA solution is withdrawn from time to time and its sulfide content was examined (Scott,1966). The gas bubbling was proceeded with unless the fancied concentration of H_2S was obtained in MDEA arrangement. The schematic diagram is shown in fig. 3.2 below:

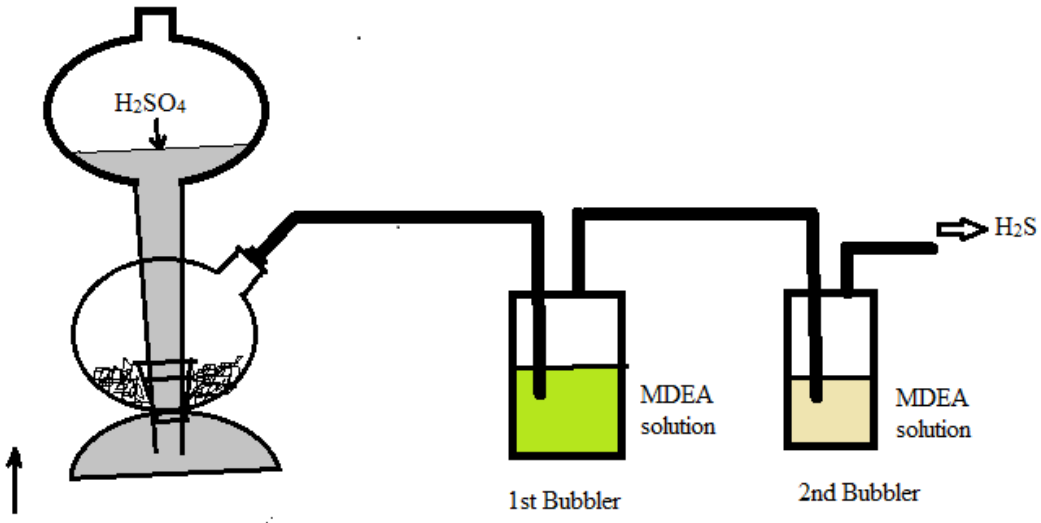


Fig.3.2 Schematic diagram of absorption of H_2S in MDEA solution

3.4 PREPARATION OF ORGANIC PHASE

Organic Phase was prepared by dissolving Chlorobenzyl chloride in toluene. Lets suppose, for setting up 2.8 M of organic phase we need to add 322.2 ml of Chlorobenzyl chloride in 677.8ml of toluene. Also, 322.2ml of benzyl chloride corresponds to 354.42gm of benzyl chloride(density=1.1g/ml) which is equivalent to 2.8 moles of Chlorobenzyl chloride. The aggregate volume of solution is 1 litre, and subsequently the strength of organic phase is 2.8M.

3.5 EXPERIMENTAL PROCEDURE

In a typical experimental run, 50 cm^3 of aq. phase containing a known concentration of sulfide is charged into the three neck batch reactor. The measure of catalyst needed is weighed and fed into the reactor by the assistance of a funnel. After that, 50 ml of organic phase of known concentration of benzyl chloride was added to the reactor. The reaction mixture was then agitated at consistent stirring rate. On regular time interval of 30 min, 60 min,120 min,180 min,240 min,360 min, 0.5 ml of organic phase was taken for analysis in the wake of allowing the reaction to stop and allowing the phase separation to happen.

3.6 ANALYSIS

3.6.1 ANALYSIS OF ORGANIC PHASE

Each organic sample was analysed by the assistance of gas liquid chromatography(GLC) utilizing a 2m long and 3mm in diameter stainless steel column. A Flame Ionization Detector (FID) was used with Helium as the carrier gas. Helium gas flow rate is kept at 0.8 bar; infusion temperature was kept at 2500 ^{0}C and indicator temperature was 3000 ^{0}C. Oven system is situated in a manner that oven is kept up at 1500 ^{0}C for 2min and afterward it is heated upto 3000 ^{0}C at the rate of 200 C/min and 3000 ^{0}C is kept up for 4 min.

%Conversion = ((Ca0 –Ca)/Ca0) * 100%.

Ca0 = Initial concentration

Ca = Final concentration

%Selectivity of Bis(4-chlorobenzyl)sulfide = (moles of Bis(4-chlorobenzyl)sulfide formed/ moles of CBC converted)*100%.

3.6.2 DETERMINATION OF SULFIDE CONTENT

Initial sulfide concentration was controlled by standard iodometric titration technique as given below:

1.) Preparation of standard (0.1M) Sodium Thiosulphate solution:

- ✓ 25 gm of sodium thiosulphate pentahydrate was added in distilled water and the volume of the solution was made upto 1litre. The atomic mass of $Na_2S_2O_4.5H_2O$ is 248 gm
- ✓ 2-3 drops of chloroform was added to keep the solution for 1-2 days.

2.) Standardization of $Na_2S_2O_4.5H_2O$ by standard KIO3 solution:

- ✓ 25ml of 0.025 molar KIO3 was taken and 1 gram of excess KI was added to it took after by adding 3ml of 1M sulphuric acid.

$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3H_2O + 3K_2SO_4$ (1)

- ✓ The iodine liberated was titrated with thiosulphate arrangement. At the point when the color of solution changed to light yellow, it was dilluted to 200ml by mixing distilled water .

- ✓ Then, around 2-3 drops of 2% by weight of starch solution was added to the dilluted solution.The shading of arrangement changed from light yellow to blue. At that point titration was proceeded till the color of the solution changed from blue to colourless.

  $2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$ (2)

- ✓ Hence, from the above reaction, it can be seen that for each 1mole of KIO3, 6 moles of $Na_2S_2O_3$ are engaged.

So,

Strength of $Na_2S_2O_3$ solution = (6*strength of KIO_3*volume of KIO_3)/volume of $Na_2S_2O_3$

3.) Preapration of 0.025M KIO_3 solution:

- ✓ 4.28gm of KIO_3 was measured and added to distilled water and the volume of arrangement was made upto 1litre.

4.) Estimation of Sulphide concentration:

- ✓ Firstly, 1ml of the concentrated sulfide solution is taken and weakened to 100 ml.

- ✓ Then, 15ml of standard (0.025M) KIO_3 arrangement is taken in a cone shaped flask.10 ml of dilute sulfide solution was taken and added to the conical flask.
- ✓ 10 ml of 10M NaOH solution was added to the conical flask.

- ✓ The mixture was tenderly bubbled for around 10min till the shading of mixture changed from white to colourless.

Thereafter, 5ml of 5%(by wt) of KI solution and 20ml of 4M sulphuric acid was added to the mixture. The generated iodine was titrated with standard sodium thiosulphate solution, which was equivalent to the unused KIO_3 solution. The potassium iodate in the basic medium oxidizes the sulfide to sulfate as given by the reaction:

$$4IO_3\text{-}+6OH^-+3S_2\text{-} \rightarrow 3SO_2^- + 4I^- +6H_2O$$

From this reaction, we can deduce that 4mole of iodate ions is equivalent to 3 moles of sulfide ions.

Hence,

H2S concentration = [15* Siodate-(Vthiosulphate* Sthiosulphate)/6]*(3/4)*(100/10)

Siodate = Strength of KIO_3

Vthiosulphate = Volume of thiosulphate

Sthiosulphate = Strength of thiosulphate

Fig. 3.3 Kipp's apparatus

3.7 REACTION OF 4-CHLOROBENZYL CHLORIDE WITH H_2S RICH METHYL DIETHANOLAMINE USING PHASE TRANSFER CATALYST

.

This is the centre reaction of the project. The effect of various parameters on the synthesis of bis(4-chlorobenzyl)sulfide and Chlorobenzyl mercaptan from the reaction of H_2S rich Methyl diethanol amine and Chlorobenzyl chloride in the presence of Ethyl triphenyl phosphonium bromide. The parameters studied are Reactant variation, Catalyst loading, Temperature variation and stirring speed of the impeller.

In many oil Industries, H_2S gas is expelled from different gas streams by dissolving in alkanol amine solution. The alkanol amine is regenerated in stripper and the H_2S gas so acquired is utilized for creating basic sulfur by using clauss process. This methodology consumes a lot of energy in stripping and various other steps and is costly as well. So, if this H_2S rich amine can be utilized for creating diverse significant chemicals, then it would of great value in refineries as H_2S is delivered in huge scale here. So, these variations are done to find the most economical way of treating H_2S and synthesize useful products using H_2S.

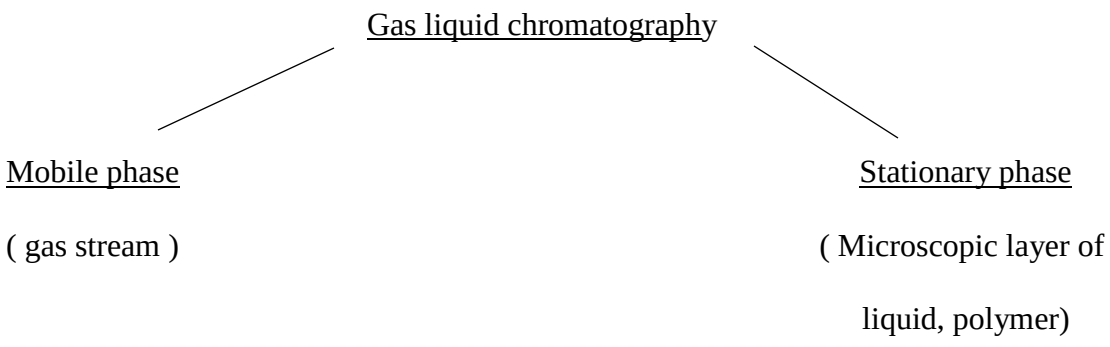
$$C_6H_5CH_2Cl_2 + H_2S \rightarrow (C_6H_5)_2SCl_2 + C_6H_5SHCl$$

Reaction of Chlorobenzyl Chloride and H2S rich MDEA to form Bis(4-chlorobenzyl)sulfide.

3.8 ANALYSIS

Gas Liquid Chromatography:

Gas liquid Chromatography(GLC) is a method by which we can determine the qualitative and quantitative measurement of complex mixtures of volatile substances. The separation process of the mixture gives the test of purity of a substance. In GLC , Helium is generally used as the carrier gas as it is an inert gas. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support. The gaseous compounds interact with the walls of the column, which causes each compound to elute at different time, which is known as retention time of the compound. Gas liquid chromatography is almost similar to Fractional distillation as both process basically separate the components of any mixture by the difference the their boiling points. However, GLC can be used on a microscale level.



Gas Chromatography graph:

The peaks given in the graph shows the percentage of the components of the reactants and products in the analyzed solution. Tall peak represents more % of that component in the solution.

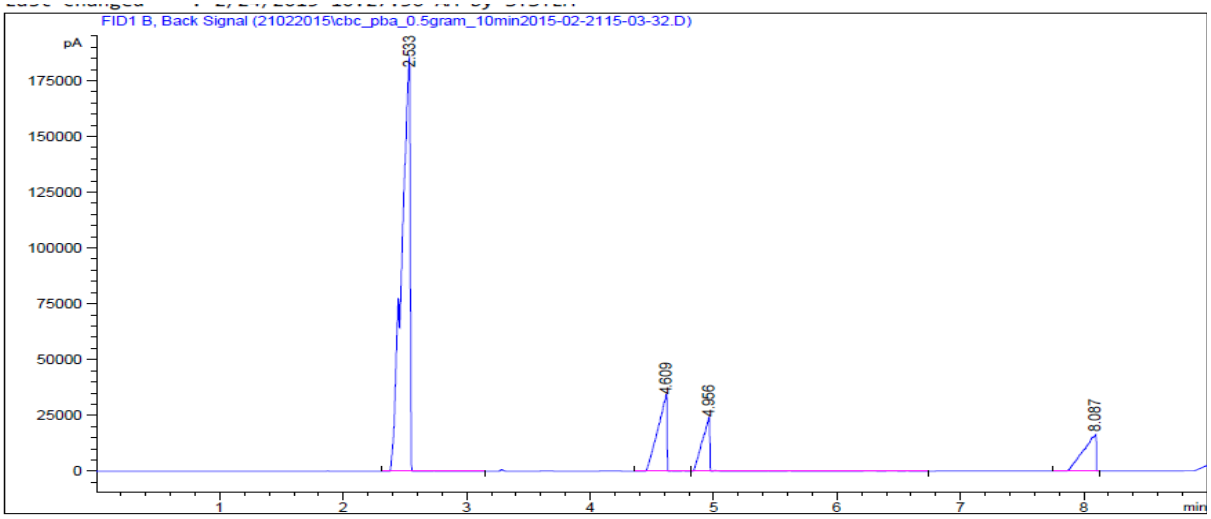


Fig. Graph obtained from GLC

3.8.1 PARAMETRIC STUDY

3.8.1.1 Effect of agitation speed:

Generally, when we increase the stirring speed of a batch reactor then as a result the reaction rate also increases. Similarly, in the above reaction the rate of reaction increase with the increase in the stirring speed.

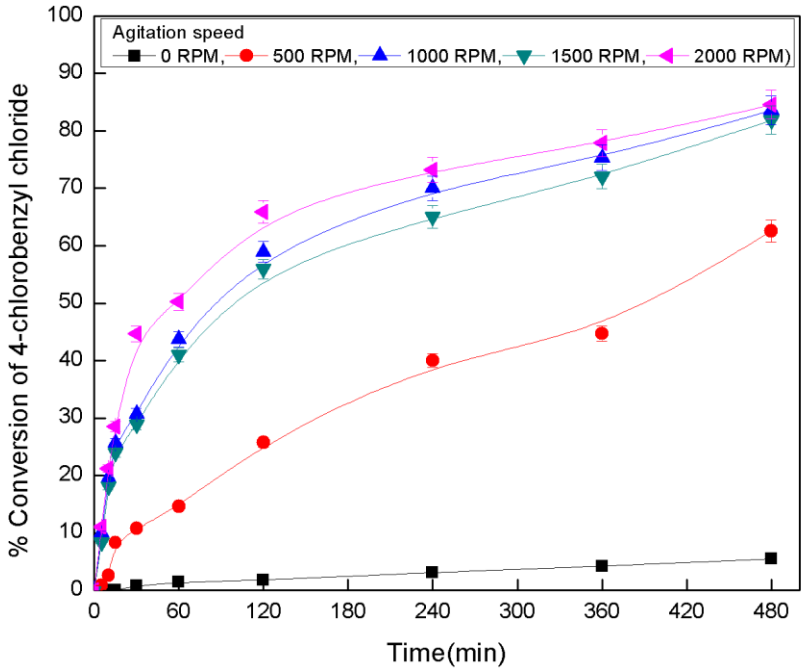


Figure 3.1 : Effect of agitation speed on CBC conversion

Aqueous and Organic Phase Volume = 50 × $10^{-5}$$m^3$ each, Sulfide Conc. = 2 kmol/m^3Aqu. Phase, CBC moles = 0.234 mol, ETPB = 0.04 kmol/m^3 org. phase, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

Result : At 1500 rpm , we have the maximum conversion.

3.8.1.2 *Effect of variation of reactant*

The effect of concentration of Chlorobenzyl chloride on its conversion and selectivity of DBCS are studied at four different concentrations in the range of 10 ml- 25 ml of Chlorobenzyl chloride or the molar range is 0.78-20 Kmol/m^3. From the following data and graph obtained from GLC analysis and Origin software, we can predict that conversion of Chlorobenzyl chloride decreases with increase in concentration.

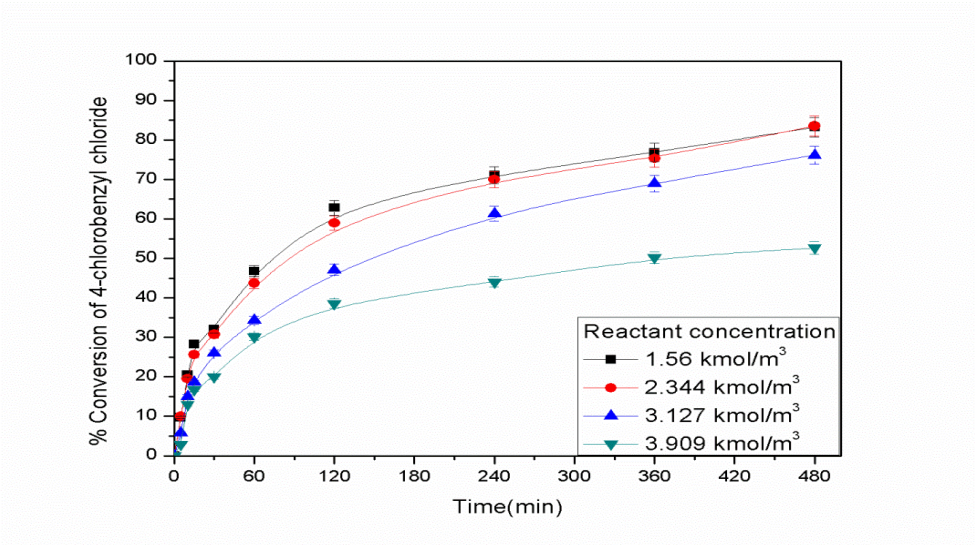


Fig.3.2 Graph for conversion %

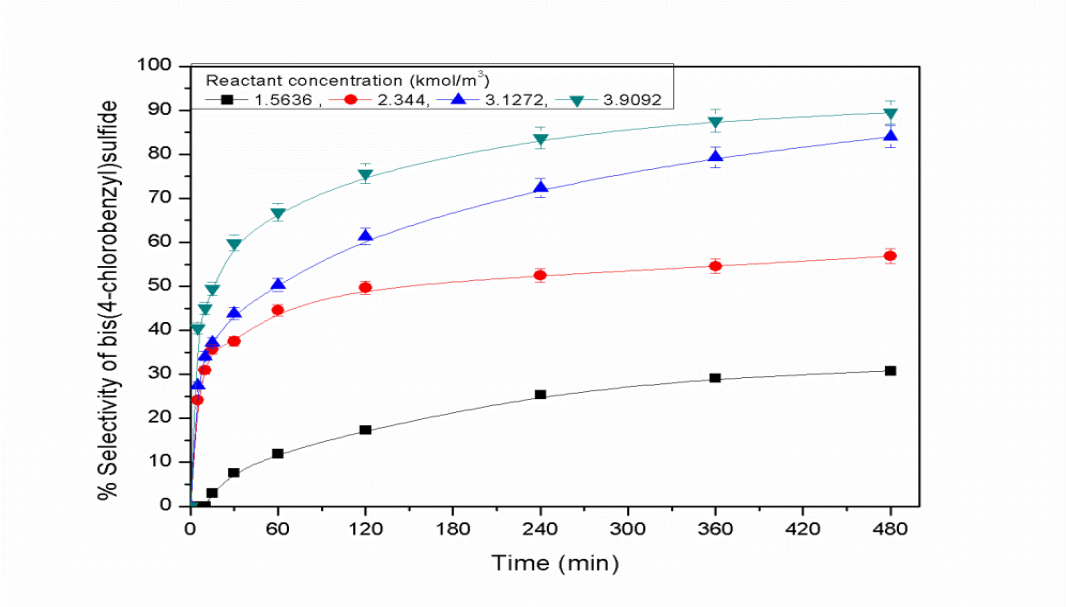


Fig.3.3 Graph for % selectivity

Figure 3.2,3.3 : Effect of CBC Concentration on (a) CBC Conversion (b) Bis(4-chlorobenzyl)sulfide Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, Sulfide Conc. = 2 kmol/m^3Aqu. Phase, ETPB = 0.04 kmol/m^3 org phase, Agitation speed= 1500 rpm, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

Graph:

From the given data we obtain a graph using Origin 8 software and we find that at 15 ml concentration of Chlorobenzyl Chloride we get the maximum conversion.

Result:

When we analyse the data, we can conclude that we can obtain maximum conversion % when the concentration of Chlorobenzyl Chloride is 3.127 Kmol/m^3 and for maximum selectivity it is also 3.127 Kmol/m^3

3.8.1.3 *Effect of catalyst loading:*

The effect of catalyst loading is studied at four different catalyst concentrations viz. 0.001 mol, .002 mol, .003 mol, .004 mol. If we increase the catalyst concentration, the conversion of chlorobenzyl chloride as well as reaction rate increases. Further, the selectivity of DBS increases with increase in catalyst concentration.Therefore, the selectivity of BM decreases Catalyst loading.

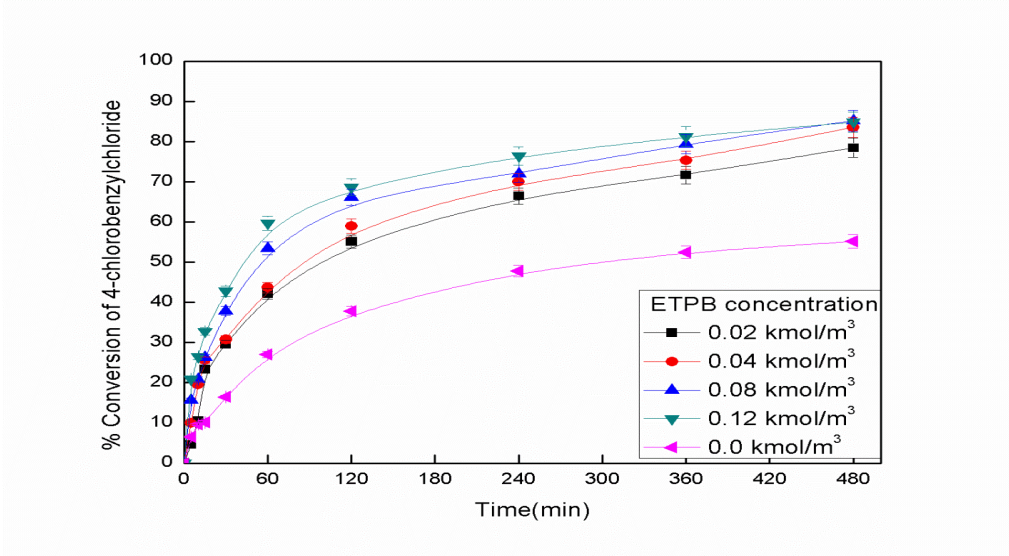


Fig.3.4 Graph for % Conversion

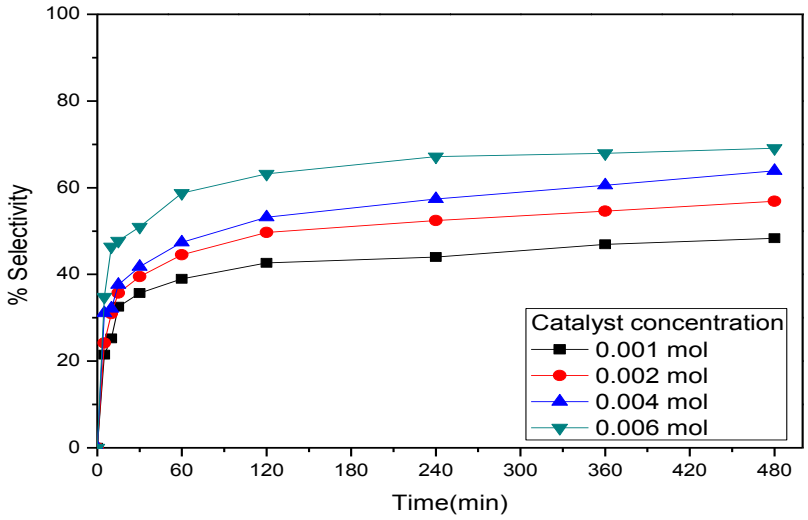


Fig.3.5 Graph for % Setectivity

Figure: Effect of ETPB Concentration on (a) CBC Conversion (b) Bis(4-chlorobenzyl)sulfide Selectivity Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, Sulfide Conc. = 2 kmol/m^3Aqu. Phase, Agitation speed= 1500 rpm, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

Observations: By analyzing the data obtained from the GLC we can infer that the conversion % increase with the increase in catalyst concentration as shown in the table.

Graph: From the above data we can obtain the graph using Origin 8 software. At 0.002 mole of ETPB we get the optimum conversion.

Result: The conversion % and selectivity of Dibenzyl Chloride Sulfide increases with the increase in catalyst concentration. Thus, from the experiment we can conclude that at 0.002 mol of catalyst we obtain the maximum conversion. This is because the other three values are close to each other and deviated from 75.77 %.

3.8.1.4 *Effect of temperature variation:*

As we increase the temperature of the reaction mixture, we observe an increase in the conversion% and selectivity of the desired product. The graph of a typical experimental run is shown below.

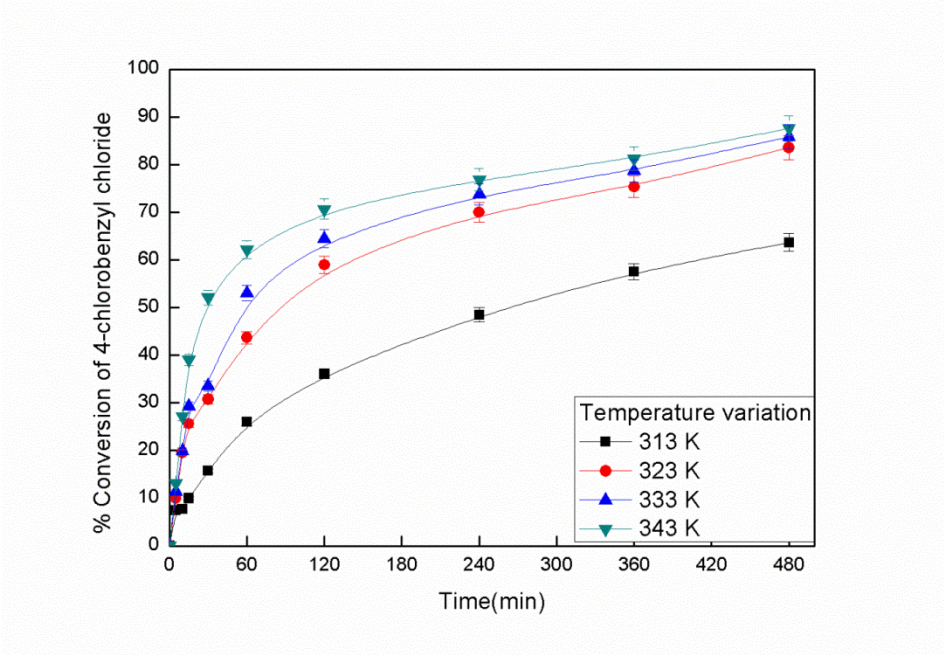


Fig.3.6 Graph for % conversion

Figure 3.6 Effect of Temperature on (a) CBC conversion

Aqueous and Organic Phase Volume = 50 × 10^{-5} m^3 each, Sulfide Conc. = 2 kmol/m^3Aqu. Phase, CBC moles = 0.234 mol, ETPB = 0.04 kmol/m^3 org phase, Agitation speed = 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

Arrhenius plot:

Arrhenius equation- $K=A(exp)^{-E/RT}$

So, slope of graph of K vs 1/T will be E/R.

Or, Slope= -E/R

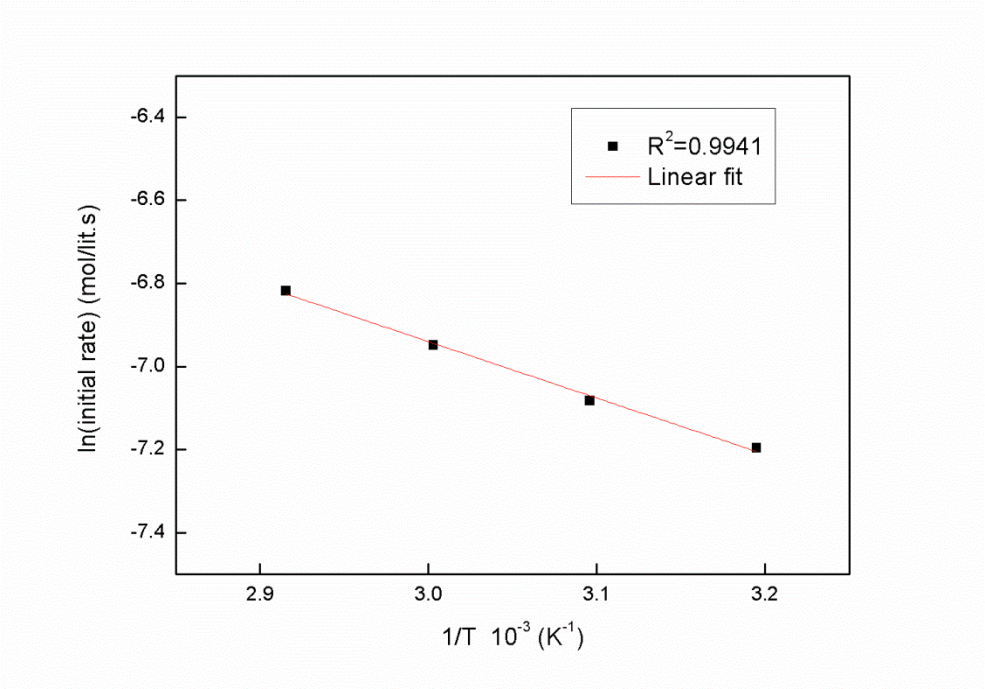


Figure.3.7: Arrhenius plot (activation energy=11.28 kj/kmol)

Result : At 373 K , we get the maximum conversion so we operate at 50^0C

3.8.2 REACTION MECHANISM

The reaction system mainly relies on upon the lipophilicity of the catalyst. In the event that the catalyst is profoundly lipophilic it implies that it can break up in both the phases that is in aqueous and organic phases and subsequently they will follow interfacial mechanism. At the

same time, if the catalyst is not lipophilic then it won't break up in both the phases and consequently they will follow extraction mechanism. The Ethyl triphenyl phosphonium bromide(ETPB) is a strong catalyst and is not soluble in any phase so it will follow extraction mechanism. In any case, it was watched that the gel globules swells. The beads stay in organic phase and ammonium ion stays in aq. phase. Since the neucleophilicity of sulfide particle and hydrosulphide particle is more than that of the chloride particle introduce in the catalyst, it replaces chloride particle on the catalyst. The accompanying reaction happens:

In the aqeous phase, catalyst swells and the negative chloride particle on the catalyst is exchanged by HS^- and S_2^- particle of the aqueous phase. The Interphase reaction takes place as:

Reaction at interface:

$$Q^+Cl^- + HS^- \longrightarrow QSH + Cl^-$$

$$2Q^+Cl^- + S^{2-} \longrightarrow QSQ + 2Cl^-$$

The polymeric microsphere bearing the active ion pairs when it reaches the bulk organic phase then it release nucleophilic species:

$$QSH \longrightarrow Q^+ + HS^-$$

$$QSQ \longrightarrow Q^+ + QS^-$$

$$QS^- \longrightarrow Q^+ + S^{2-}$$

Due to the reaction of 4-chlorobenzyl chloride with HS- and S2- produces DBCS and CBM.

$$C_6H_5CH_2Cl_2 + HS^- \rightarrow C_6H_5CH_2SHCl + Cl^-$$

$$C_6H_SCH_2Cl_2 + C_6H_5CH_2SHCl \rightarrow Cl\ C_6H_5CH_2SCH_2C_6H_5Cl + HCl$$

The discharged chloride ion combines with Q+ and the catalyst is recovered. From the concentration profile of an ordinary run,it is seen that the concentration of chlorobenzyl mercaptan ascends to a maximum and decreases. Whereas, the concentration of DBCS continues consistently increasing. From this we can conclude that the Chlorobenzyl mercaptan combines with Chlorobenzyl chloride to deliver dibenzyl chloride sulfide and HCl. Since CBM is the weak acid so this reaction is slow. This HCl produced reacts with MDEA to form methanol amine hydrochloride.

Operating Conditions: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of chlorobenzyl chloride – 2.8M, Sulphide concentration – 2.3M, MEA/H2S ratio – 2.1,, Catalyst loading – 10%(w/v), Temperature - 320C, , Stirring speed – 1500 rpm.

CHAPTER 4

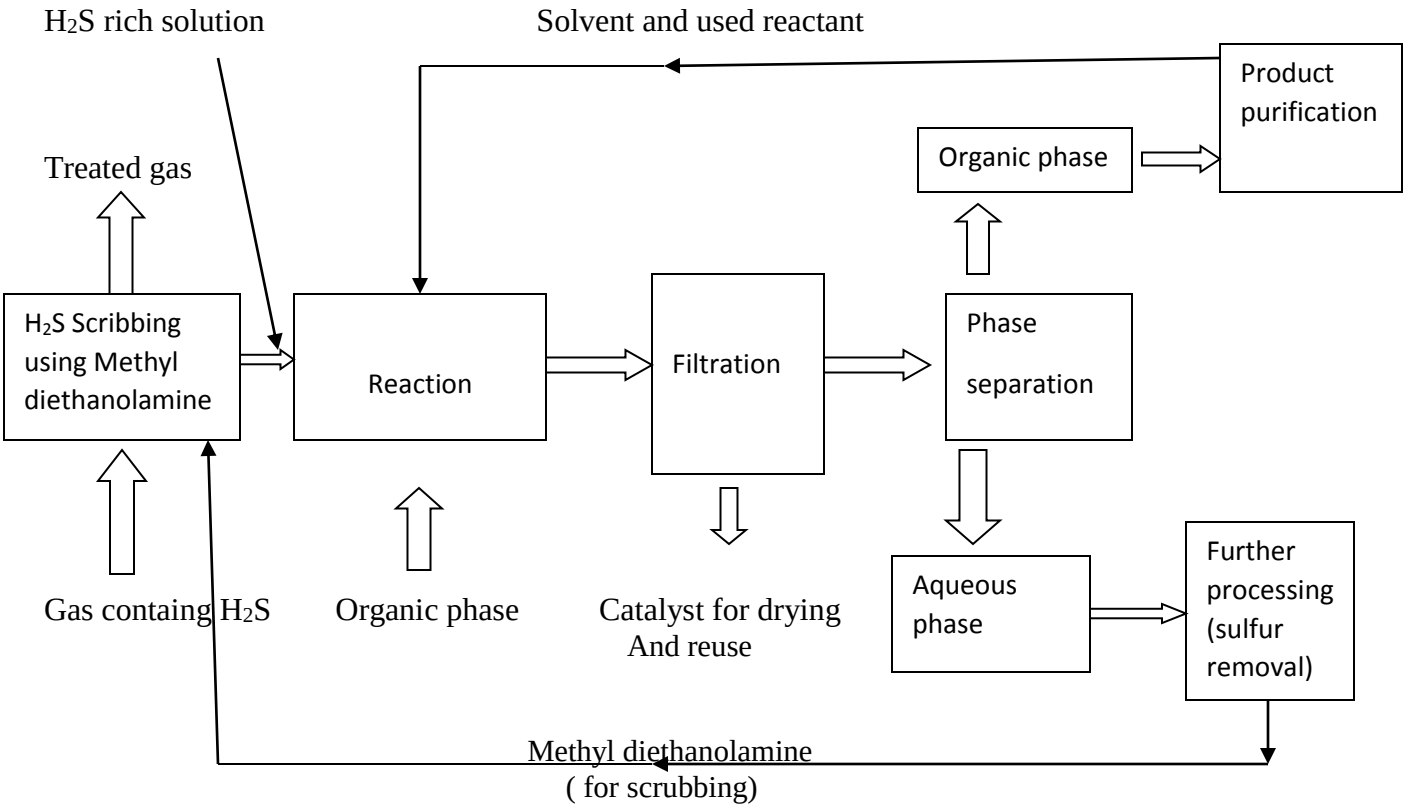
SUMMARY AND CONCLUSION

4.1 SUMMARY OF THE PROJECT

The work done in this thesis has led to the development of an industrial process for generation of dibenzylchloride sulphide and chlorobenzyl mercaptan using hydrogen sulphide gas present in various byproduct gas streams. According to the present process, HS present in the gas stream can be used for the production of DBCS and CBM in two steps:

- Removal of H_2S gas from the gas stream by absorbing it in monoethanol amine solution.
- Second step involves the production of DBCS and CBM using the H_2S rich MDEA obtained from the first step.

The present process is shown in the following scheme 4.1.



Schematic representation of the process

4.2 CONCLUSION

The reaction of H_2S rich MDEA and Chlorobenzyl chloride present with toluene as solvent created DBCS and CBM which is all that much significant. One can specifically get DBS by keeping the starting sulfide content high, long reaction time and high Chlorobenzyl chloride conversion. In this process, the two active ion sets QSQ and QSH moved from the aqueous phase to the organic phase where it forms DBCS and CBM. The most extreme conversion of 90% and maximum selectivity of 46 % has been found. It needs further treatment as the complete usage was not watched even after 6 hours, so some sulfide probably stayed inside the MDEA arrangement. The selectivity is low, this may be because of the reason that reaction is not

happening at high temperature. There is around 21.6% fall in catalytic activity even after 4 cycles of utilization. So this catalyst can be industrially extremely important for this procedure.

4.3 SCOPE FOR FUTURE WORK

The mechanistic pathway demonstrated in Chapter 3 is taking into account some prior studies and information. Aqueous can likewise be examined to know the ions present in it and to think about mechanistic pathway of the triphasic system.

Effect of other variations:

Effect of variation of Sulfide content can be studied to observe the reaction kinetics as it is very important for the modeling of the process. This can help in increasing the conversion and decreasing the use of catalyst, reaction time. The impact of pH can be studied on as concentration of S_2^- and HS^- has vital part to play in the selectivity. The concentrations of sulfide and hydrosulphide particle rely on pH. In the present study, toluene has been utilized as a solvent and swelling was seen in the catalyst. The solvent plays a critical part on PTC reaction, as it influences the transport properties of PTC and dynamic catalyst species (QSH and QSQ). Different sorts of solvent like chlorobenzene, n-heptane can be utilized.

The aqueous phase utilized as a part of the present work is MDEA which can retain both CO_2 and H_2S. Our present work is applicable for the stream containing H_2S and CO_2, just if the aqueous phase is H_2S specific.

REFERENCES

REFERENCES

Heather, J.B. Method for Preparation of Benzyl Mercaptan. U.S. patent No. 4740623, 1988.

Kaewsichan, L.; Al-Bofersen, O.; Yesavage, V. F.; Selim, M. S. Predictions of the solubility of acid gases in monoethanolamine (MEA) and methyldiethanolamine (MDEA) solutions using the electrolyte-UNIQUAC model. Fluid Phase Equilibria 2001, 183–184, 159-171.Khuri, A.I.; Cornell, J.A. Response Surfaces: Design and Analyses, Dekker, New York. .

Hydrogen sulfide: Overview, National Pollutant Inventory, Australia

Kohl, A.L.; Nielsen, R.B. Gas purification, Gulf Publishing Company Houston, Texas,1997.

Labat, Y. Synthesis of Benzyl Mercaptan. European Patent No. EP0337838, 1989.

Maity S.K; Pradhan N.C; Patwardhan . Reaction of benzyl chloride with ammonium sulfide under liquid–liquid phase transfer catalysis: Reaction mechanism and kinetics, Journal of Molecular Catalysis A: Chemical 250 (2006) 114–121.

Al-Baghli, N. A.; Pruess, S. A.; Yesavage, V. F.; Selim, M. S. A Rate-based Model for the Design of Gas Absorbers for the Removal of CO2 and H2S Using Aqueous Solutions of MEA and DEA. Fluid Phase Equilibria 2001, 185, 31-43.

Wang, D. H.; Weng, H. S. Preliminary Study on the Role Played by the Third Liquid Phase in Phase Transfer Catalysis. Chemical Engineering Science 1988, 43, 2019-2024.

Wang, M.L.; Wu, H.S. Kinetic and mass transfer studies of a sequential reaction by phase transfer catalysis. Chemical Engineering Science 1991, 46 (2), 509–517.

Austgen, D. M.; Rochelle, G. T.; Peng, X.; Chen, C. Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL Equation. Industrial & Engineering Chemistry Research 1989, 28, 1060-1073.

Bittell, J. E.; Speier, J. L. Synthesis of Thiols and Polysulfides from Alkyl Halides, Hydrogen Sulfide, Ammonia, and Sulfur. Journal of Organic Chemistry 1978, 43(9), 1687-1689.

Sidi-Boumedine, R.; Horstmann, S.; Fischer, K.; Provost, E.; Fürst, W.; Gmehling, J. Experimental determination of hydrogen sulfide solubility data in aqueous alkanolamine solutions. Fluid Phase Equilibria 2004, 218, 149-155.

Vallée, G.; Mougin, P.; Jullian, S.; Fürst, W. Representation of CO2 and H2S Absorption by Aqueous Solutions of Diethanolamine Using an Electrolyte Equation of State.Industrial & Engineering Chemistry Research 1999, 38, 3473-3480.

Weiland, R. H.; Chakravarty, T.; Mather, A. E. Solubility of Carbon Dioxide and Hydrogen Sulfide in Aqueous Alkanolamines. Industrial & Engineering Chemistry Research 1993, 32, 1419-1430.

Yadav G.D.; Naik S.S. Clay-Supported Liquid-Liquid-Solid Phase Transfer Catalysis: Synthesis of Benzoic Anhydride. Organic Process Research & Development 2000, 4, 141-146.

Yang, H.M., Lin, C.L. Phase-transfer catalyzed benzylation of sodium benzoate using aliquat 336 as catalyst in liquid–liquid system. Journal of Molecular Catalysis A: Chemical 2003, 206, 67–76.

Maity S.K.; Sen S.; Pradhan N.C.; Patwardhan A.V. Utilization of hydrogen sulphide for the synthesis of dibenzyl sulphide:Effects of process parameters on conversion and selectivity. Int. J. Chem. Sci.: 5(4), 2007, 1569-1578.

Harvey, W. W.; Makrides, A.C. Process for Removing Hydrogen Sulfide and Ammonia from Gaseous Streams. Patent No. US4192854, 1980.

Melville, J. B.; Goddard, J. D. A Solid-Liquid Phase-Transfer Catalysis in Rotating-Disk Flow. Industrial &. Engineering Chemistry Research 1988, 27, 551-555.

Plummer, M.A. Process for Recovering Sulfur and Hydrogen from Hydrogen Sulfide. Patent No. WO9412431, 1994.

Robin, P. Method for Removing Hydrogen Sulfide From Natural Gas. Patent No. WO9964137, 1999.

Sen S.; Pradhan N.C; Patwardhan . Kinetics of reaction of benzyl chloride with H2S-rich aqueous monoethanolamine: selective synthesis of dibenzyl sulfide under liquid–liquid phase-transfer catalysis, Asia-Pac. J. Chem. Eng. (2010).